

SCIENCE FOR CERAMIC PRODUCTION

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TECHNOLOGY OF CERAMICS IN THE CONTEXT OF SYNERGISM (A REVIEW)

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Synergism as an interdisciplinary science studying self-organization processes in open systems exchanging matter (energy, material, information) with the ambient medium makes it possible to consider the course of technological operations from the most general point of view. Ceramic technology can be divided into two main stages: a system in the production of a molded preform mainly accumulates energy in the form of free surfaces of particles and their volume defects, whereas in sintering the system mainly spends this energy on strengthening and consolidation of the product.

The technology of ceramics can be represented as a sum of processes subdivided into two main stages: preparatory operations with initial components resulting in the production of a preform of a certain shape and size and sintering providing for required (preset) properties and structure in the product. All process operations, from treatment of raw materials to making a finished product, are mainly directed to modifying the product structure in a desired direction, treating the structure in a broad sense as a modification of shape, size, and the composition of structural elements. A system evolves mainly via destruction of its structural elements or their deformation. Indeed, all technological processes (preparation of powders and molding mixtures, molding, removal of temporary technological binder, and sintering) to a certain extent involve a supply of mechanical and thermal energy and its dissipation in the course of destruction or deformation (except for the part of energy dissipated in the form of Joule heat). These irreversible processes take place in significantly nonequilibrium conditions and can be better understood in the context of the physics of open systems, thermodynamics of irreversible processes, or synergism [1, 2]; their elementary processes can be most completely considered in the context of the physical chemistry of crystals with defects [3, 4]. According to the synergist approach, a supply of energy to a material is accompanied by the self-organization of this material for the purpose of creating new structures or using the available structures for energy dissipation (dissipative structures) or its accumulation [5, 6].

All systems in their evolution pass through a sequence of stable and unstable states. A stable state of a system means a dynamic equilibrium with the ambient medium and is accompanied by a continuous exchange of matter (material, energy, information). A system in an unstable state acquires increased sensitivity to slight uncontrolled impacts (inner fluctuations and external disturbances) known as noises. To make the evolution of a structure predictable, it is necessary to provide a controlling signal within unstable states of the system, which exceeds the noise level. Such controlling signal can be provided by an external effect (temperature, pressure, various physical fields) or by internal disturbances caused by structural elements that have been created at preceding technological stages.

The evolution of a structure to a large extent depends on the degree of nonequilibrium of processes. At the same time, the regularities of the behavior of systems in nonequilibrium conditions conform to general descriptions, which opens up ways for using very remote analogies: equations proposed for certain processes can often be successfully applied to other processes that are very different in their physical meaning.

The crystal-chemical specifics of ceramic materials and their complex real structure (multi-level fractal-type structure [7]) are the reasons for their brittle behavior at relatively low temperatures (usually below 0.5–0.7 melting point) and destruction after a small elastic deformation [8]. As temperature grows, thermal activation generates the flow mechanism and the material exhibits a plastic deformation or a viscous flow, although relatively small. Depending on temperature, an increasing load applied to ceramics produces a nearly instant (sonic velocity in material) destruction after a slight

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elastic deformation in the case of the brittle behavior or a relatively slow destruction by accumulating a substantial irreversible deformation in the case of a viscous flow.

Actually, such deformation is due to disrupting the continuity of material, and yet contemporary definitions of plasticity ignore the need to preserve this continuity. Disturbances of continuity accompany a plastic deformation, while the article preserves its integrity at the macrolevel and the more so at microlevels and sublevels, which leads to the formation of new surfaces and the respective energy consumption. This actually means the formation of structures that effectively dissipate energy supplied from the ambient medium (in this case by accumulating the energy within the system). The physicochemical mechanism of this phenomenon is represented by the formation of lattice defects [9] which are sites with higher (compared to a defect-free crystal) energy.

The size of areas with disturbed continuity depends on the plastic or brittle properties of the material and is determined by internal and external conditions. The internal conditions primarily include the type of chemical bond and the structure of the elementary cell of the material: the higher the degree of covalence of the chemical bond and the more complex the elementary cell form (structure and number of sublattices), the more prone this material is to brittleness [7]. The external conditions include the rate of increment of an external mechanical force, the temperature variation rate, the heat removal rate, etc., including the size of the product (i.e., the scale factor sometimes plays a noticeable role). The higher the degree of deviation from equilibrium caused by external conditions, the more prone is the particular ceramic to brittleness.

In the context of this approach it is essential to note that ceramic materials have two temperature ranges in which the regularities of energy dissipation are significantly different: the range of brittle behavior and the range of plastic (viscous) behavior. Within the brittle range virtually all input energy is spent on the formation of new external surfaces, whereas within the plastic range a part of the energy is spent on the formation of inner defects (i.e., the lattice defects). In technological operations under relatively low temperatures, a plastifying additive (polymer) is usually introduced to decrease brittleness and to impart a certain plasticity to the preform in view of the risk of its destruction. Many processes use also plastic materials, in particular, clay. Let us analyze each of the specified operations with respect to their motive force, kinetics, and the influence of different factors.

Elastic deformation up to brittle destruction is used in practice for grinding initial nonplastic components [9]. According to the Le-Chatelier – Brown principle, the system (material milled) resists an external impact, and intensifying the external impact stimulates self-organization processes inside the system. For better dissipation of input energy, the system elements (particles in grinding) join in aggregates bonded by the force of adhesion: they cooperatively resist the external impact due to a certain shear deformation of particles with respect to each other. The milling of particles

joined in such aggregates is significantly decelerated, which is a negative factor. However, the purpose of the system is not to protect its particle from destruction but to dissipate the supplied energy to a maximum possible extent. In high-energy high-speed mills the system dissipates the energy flux mostly on destroying particles and other processes do not have time to occur, which intensifies the milling process.

Molding is implemented while preserving the continuity of material by realizing its plastic (viscous) deformation; destruction at this stage is inadmissible [10]. For this purpose temporary technological binders are used which, furthermore, decrease friction between powder particles. In semidry molding the binder content is minimal, which, in turn, calls for a high pressure in molding. To dissipate the input energy, skeleton structures arise in the molding powder, absorbing the main part of the external pressure and transmitting it to the mold walls. An increased binder content facilitates the possibility of plastic deformation (plastic molding). In this case as well, a dissipative structure may arise in the material, whose size is determined by the system viscosity. It should be noted that molding proceeds the most easily in the case of slip casting.

The next type of deformation is shrinkage caused by evaporation (drying) or thermal decomposition of the technological binder [11]. The drying process mechanism is the diffusion of liquid from the inner parts of the article toward its surface and then its evaporation into the gaseous phase. The motive force in this case is the binder concentration gradient from the preform volume to the external medium. The self-organization of the system leads to its splitting into isolated sites (blocks) that are dissipative structures. They allow the preform to keep its integrity due to the formation of microcracks between the blocks and the possibility of their slight displacement with respect to each other. Such blocks can be either more compact areas newly formed within the preform, or large grains or granules that are introduced beforehand into the molding mixture.

The shrinkage of the preform in removing the binder occurs as the volume of the highly concentrated suspension decreases under the effect of surface tension of the liquid. The activation of the process by supplying thermal energy intensifies self-organization inside the system. The preform structure changes to minimize the consequences of the external impact, which produces nonuniform densities or local volumetric variations. These processes actually result in the formation of dissipative structural elements (blocks) for dissipating the input energy. The negative factor in this case is the emergence of breaks in continuity (cracks) on the boundaries of new formations. To avoid such defects, grog components are normally used, which can be regarded as inner controlling signals. The grog components break the preform volume into small fragments whose boundaries are more permeable for the binding agent. This makes it possible to distribute more uniformly the stresses inside the preform and to prevent crack formation [12].

Thus, the operations of preform production considered above are based either on the brittle destruction of initial powder particles in milling, or on the plastic (viscous) deformation of the ensemble of inorganic particles in preform molding. The specifics of these processes implies the predominant creation and preservation of accumulating structures inside the system, whose energy is to be used later at the next stage of ceramic technology, i.e., in sintering. Strictly speaking, we mean the viscous flow of suspensions based on organic polymers upon introducing a temporary technological binder or the viscous flow of aqueous suspensions based on plastic mineral materials (clays). These processes in technology are known as “plastic molding,” hence, we will not treat strictly the term “plasticity.”

The final and the main technological operation in the production of any ceramics is sintering, in the course of which the quality of the finished product is determined. Actually all preparatory operations influence the course of sintering, although they are independent process stages witnessing the evolution of systems based on an ensemble of mineral particles with an inherent particular structure. The structural evolution of a ceramic article in sintering starts with the structure of the preform, which is a low-strength porous powder article composed of inorganic nonmetal particles bonded by adhesion forces. All states, stable as well as unstable ones, that have occurred in the system during the preceding operations (in other words, prehistory) influence the state of the finished product. Unstable states, where the future evolution of the system remains unpredictable and susceptible to the effect of slight uncontrolled effects (noises) [13] are especially significant. If a particular system after an unstable state under similar conditions can attain one of many steady states (multistability) that differ significantly in their characteristics, this in practice leads to poor reproducibility of the quality of the product [14]. Properly speaking, a technology can be regarded as a search for possibilities of eliminating such multistability, where individual states have significantly different properties. This can be achieved by one of two ways: either make stable states similar in their properties, or use a controlling external or internal signal to force the system after the unstable state to get into such a stable state whose parameters satisfy our purpose.

Sintering of powders constitutes their deformation (flow) under the effect of surface tension forces [15]. The motive force in sintering is excessive surface energy of powder particles compared to solid materials. Under the effect of this force, in certain sites of a porous crystalline body local vacancy flows arise from tensile to compressed zones (i.e., from concave to convex sites) in the contact of particles under thermal activation; clearly, the atom flows have the opposite direction. The consequence of these flows is spontaneous healing of pores and particle centers approaching each other; macroscopically, shrinkage deformation and growth of strength are observed. These two processes are usually combined in the general notion of “sintering,” although sometimes particle centers do not approach each other. However,

in all cases local deformation processes related to diffusion flows take place. In many ceramics a relatively low-melting vitreous phase with substantial crystal inclusions is formed under high temperatures as a result of various chemical transformations. In this case sintering proceeds similarly to merging of liquid drops; however, the apparent viscosity of such system has rather high values compared with a liquid, due to the presence of solid particles. In the context of thermodynamics of open systems, sintering represents the dissipation of excess energy of powder particles stored in accumulating systems in the course of mass transfer processes.

It is significant that phenomenologically all flow processes in molding, drying, and sintering are governed by the same regularities, since they proceed under the effect of the same motive forces and can be formally described by the same kinetic regularities. In all cases under the effect of mechanical stress we have either a viscous flow of fluids and amorphous bodies, or a diffusion-viscous flow of crystals. The difference exists only in single flow acts of fluids and amorphous bodies, on the one hand, and crystals, on the other hand. At the same time, the effective viscosity determining a flow rate can be formally represented in the form of identical dependences, in which the constants take into account the role of factors that are different in these particulars cases, including structural factors. Note that the temperature dependence of viscosity is based on the Arrhenius exponential law; indeed, the physical meaning of the activation energy and the preexponential factor differs. It should be noted that in ceramic production only the two flow mechanisms considered above are used. Thus, one can write [16]

$$\frac{\Delta l}{l_0} = K \tau^n;$$

$$K = K_0 \exp\left(-\frac{Q}{RT}\right),$$

where $\Delta l/l_0$ is shrinkage; K is the velocity constant; τ is time; $n = \text{const}$ is the index depending on the process mechanism; K_0 is the preexponential factor including activation entropy and surface tension; Q is the process activation energy; R is the gas constant; T is the temperature.

Since the major part of the physicochemical processes in various stages of ceramic production can be reduced to mass transfer, these processes can be represented in the form of the above dependences. Formally they describe the process in time at a temperature; the role of other factors is taken into account in the values of the constants. This makes it possible to propose certain approaches to organizing automated control systems to obtain ceramic products of prescribed quality, i.e., with prescribed parameters. A possible approach is as follows. Provided there are automated adjustable machines, one can design an experiment for each machine using the above formal dependences in accordance with a certain design allowing for optimizing the process (for instance, simplex design, factorial design, etc.) [17]. The results of these

experiments will provide empirical dependence coefficients for each specific process and each machine, as well as a production control program. Other operations (for instance, milling) as well can be optimized based on similar formal dependences

To conclude, it should be noted that the behavior of ceramic structures depends significantly on the mobility of their crystal lattice elements determining the mass transfer velocity; this mobility, in turn, is determined by thermal activation. At relatively low temperatures (around 0.5–0.7 melting point) the dissipation of input energy by developing corresponding structures through diffusion mass transfer is very slow, therefore, dissipation is mostly implemented by already existing elements. As the structure evolves in an external force field, for instance, under sintering, the type of the dissipative element at different stages can vary in accordance with the process kinetics, which determines the kinetics of the evolution of dissipative structures. Note that these processes in ceramics are slow even at temperatures close to the melting point.

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